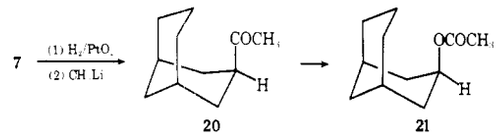
(5) T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **35**, 4109 (1970).
(6) No information concerning the conformational preferences of compounds **7–14** is meant to be implied by the indicated structures.
(7) M. Fisch, S. Smallcombe, J. C. Gramain, M. A. McKervey, and J. E. Anderson, *J. Org. Chem.*, **35**, 1886 (1970).
(8) Ketone **10** also can be obtained by heating 3-*endo*-acetylbicyclo[3.3.1]-nonane (**20**) in a sealed ampule at 200–205 °C. Ketone **20** is readily prepared from acid **7**. Catalytic hydrogenation of **7** gives 3-carboxybicyclo[3.3.1]nonane[13] which undergoes reaction with methyllithium to provide **20**. The skeletal framework of **20** and the skeletal position and stereochemistry of the acetyl group in **20** were firmly established by its oxidation with *m*-chloroperbenzoic acid to give the previously reported 3-*endo*-acetoxybicyclo[3.3.1]nonane[7] (**21**).
(9) Since **8** → **9** is acid-catalyzed, ketone **8** can be converted "directly" to epimerized ketal **12** by reaction of **8** with ethylene glycol containing a trace of *p*-toluenesulfonic acid.
(10) H. Langhals and C. Ruechardt, *Chem. Ber.*, **108**, 2156 (1975).
(11) For examples see: R. C. Fort, Jr., "Adamantane: The Chemistry of Diamond Molecules", Marcel Dekker, New York, N.Y. 1976.
(12) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley-Interscience, New York, N.Y., 1967, p 1000.
(13) T. Sasaki, S. Eguchi, and M. Mizutani, *J. Org. Chem.*, **37**, 3961 (1972).



20 21

syn- and *anti*-Tricyclo[4.1.0.0^{2,4}]heptan-5-one

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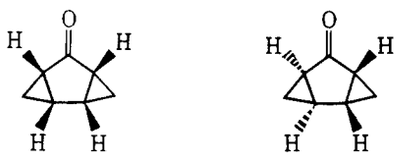
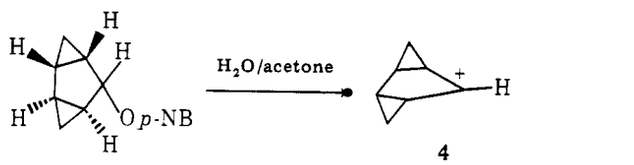
The synthesis, isolation, and spectroscopic characterization of the epimeric ketones *syn*- and *anti*-tricyclo[4.1.0.0^{2,4}]heptan-5-one (**1** and **2**) are described. Two synthetic schemes lead to a nearly equimolar mixture of **1** and **2**, while a third yields **2** almost exclusively. The syn isomer **1** proved much more labile compared to the anti isomer **2**. Complete assignments of protons in the NMR spectra were made possible by a study of lanthanide-induced chemical shift modifications.

The epimeric ketones *syn*- and *anti*-tricyclo[4.1.0.0^{2,4}]-heptan-5-ones (**1** and **2**) are of interest as precursors of the



1 2

epimeric carbene species *syn*- and *anti*-tricyclo[4.1.0.0^{2,4}]-heptan-5-ylidenes[2] and as precursors of the carbonium ion species *syn*- and *anti*-tricyclo[4.1.0.0^{2,4}]hept-5-yl cations. The anti ketone **2** had earlier been synthesized by Gajewski and Shih and was utilized in an investigation of the properties of anti cation **4** as generated by the solvolysis of **3**.[3] **3** was found



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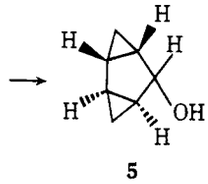

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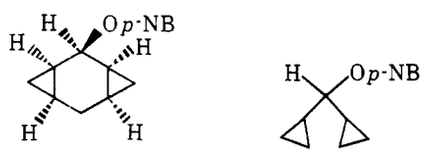
to be significantly less reactive than the model compounds **6** and **7**. We wish to report the details of the synthesis of the syn ketone **1** along with the total spectroscopic characterization



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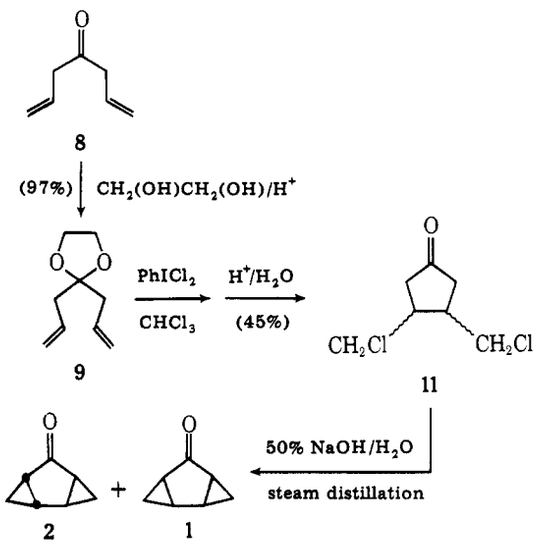
7

Scheme I



of both the syn and anti isomers and a discussion of their relative chemical properties.

Synthetic Methods. Three synthetic schemes were developed and successfully pursued for the preparation of **1** and **2**. Scheme I began with the known diallyl ketone **8**.[4] Ketalization and treatment of the ketal **9** with iodobenzene dichloride[5] led, after hydrolysis, to a mixture of *cis*- and *trans*-3,4-bis(chloromethyl)cyclopentanones (**11**). Treatment of **11** with 50% aqueous NaOH followed by steam distillation resulted in a mixture of products which proved to be 52 and 48% *syn*- and *anti*-tricyclo[4.1.0.0^{2,4}]heptan-5-one, respectively. Gajewski's synthesis of **2** also involved a cyclization process such as that used to convert **11**.[3] In their final step they converted a pure trans ditosylate into **2**.

Scheme II employed a sequence which appeared to be somewhat more convenient. Drawing on the analogues provided by Doering[6] and Gutsche[7] in performing intramolecular trapping of keto carbenoids by a remote double bond, a se-

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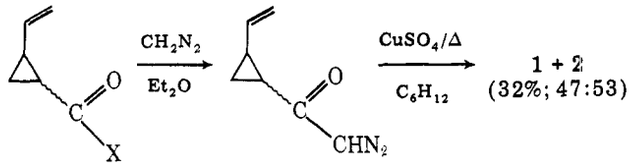
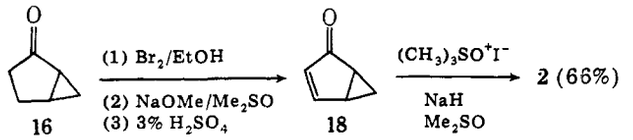
Scheme II



12, X = OEt
13, X = OH
14, X = Cl

15

Scheme III

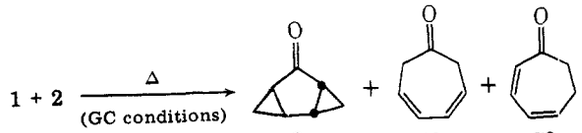


16 **18**

quence was devised utilizing a mixture of *cis*- and *trans*-ethyl 2-vinylcyclopropanecarboxylate (**12**) as starting material.[8] Treatment of acid chloride **14** with ethereal diazomethane afforded a mixture of *cis*- and *trans*-1-diazomethylketo-2-vinylcyclopropanes (**15**) as evidenced by the strong IR band at 2100 cm^{-1} and the diazomethyl singlet at δ 5.31 in the NMR spectrum. Copper-catalyzed decomposition of **15** in refluxing cyclohexane produced a 32% yield of isomeric tricyclic ketones **1** and **2** in a ratio of 47:53.

Scheme III, while not providing a satisfactory route to the syn ketone **1**, did result in an interesting source of **2**. The starting material in Scheme III was bicyclo[3.1.0]hexan-2-one (**16**), which could be synthesized from either 4-tosyloxycyclohexanone[9] or 2-cyclopentenone.[10] Bicyclo[3.1.0]hex-3-en-2-one (**18**) was prepared from **16** employing the procedure of Russell and Stevenson,[11] with some modification. The treatment of **18** with trimethylsulfoxonium ylide afforded **1** and **2** in a ratio of 2:98.

Isolation of the Pure Isomeric Ketones. Detection and isolation of **1** and **2** proved initially troublesome using normal GC. An injection of the isomeric mixture of ketones onto various Carbowax 20M columns at 130–160 °C typically resulted in the isolation of *three* isomeric ketones, none of which proved to be the syn isomer **1**.



2 **19** **20**

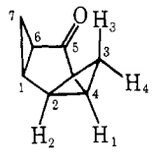
The anti tricyclic ketone **2** was identified by comparison of its ^{1}H NMR spectrum with that reported by Gajewski and Shih.[3] The outstanding feature of this NMR spectrum (100 MHz) is the unsymmetrical two-proton quartet (J = 3.5 Hz) at δ 0.85. The remainder of the spectrum consisted of three two-proton multiplets centered at δ 1.25, 1.56, and 2.08. The IR (1720 cm^{-1}), UV [λ_{max} 287 nm (ϵ 28)], and mass spectra [m/e 108 (M$^+$)] were also confirmative of the structure. The other two products proved to be 2,4- and 3,5-cycloheptadienones, which were recognizable by the four-proton multiplet at δ 3.00 for the 3,5 isomer.[12] These products were accounted for by an acid-promoted rearrangement of the entire syn ketone and part of the anti ketone. Previous work by Borg and Kloosterziel had shown that the cycloheptadienones were interconvertible in the temperature range of 60–100 °C via a facile 1,5-hydrogen shift, resulting in an equilibrium mixture dominated by the 2,4 isomer.[12]

Isolation of analytically pure **1** and **2** was accomplished by the use of an *alkaline* column (10% Carbowax 20M) using 3.5% KOH to effectively remove active sites from the inert support, typically Chromosorb P (regular). Whereas liberal injections of ammonia had not proved successful, the KOH-coated column allowed for almost quantitative separation and isolation of **1** and **2** in the temperature range of 130–165 °C. However, at temperatures above 180 °C, almost complete destruction of the syn isomer was observed.

The *syn*-tricyclo[4.1.0.0^{2,4}]heptan-5-one gave rise to four complex two-proton multiplets in its 100 MHZ NMR spectrum at δ 0.76, 1.50, 1.78, and 2.18. The multiplets at δ 1.50 and 1.78 were overlapping, a feature which readily distinguishes **1** from **2**. Its IR (1700 cm^{-1}), UV [λ_{max} 283 nm (ϵ 70)], and mass spectra [*m/e* 108 (M$^+$)] were also consistent with the structure.

Silica gel chromatography conveniently afforded separation of larger quantities of **1** and **2**. Both **1** and **2** could readily be converted to their tosylhydrazones, with **1** being converted in 83% and **2** in but 31% yield.

Lanthanide-Induced Chemical Shift Studies. A concluding aspect of analysis of **1** and **2** derived from an attempt to assign their various NMR proton absorptions. Employing Eu(fod)$_3$, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)europium(III), lanthanide-induced shifts produced some rather interesting spectral changes, the most interesting of which demonstrated that the two protons adjacent to the carbonyl function (α-methine cyclopropyl protons) in both **1** and **2** were *not* located farthest downfield in the NMR spectra. It appeared that the protons most deshielded in these systems were the two protons located at C$_1$ and C$_2$, the β-methine cyclopropyl protons. Further, calculations of the agreement factor R[13] for the four types of protons present afforded values of 0.16 and 0.23 for **1** and **2**, respectively. Also



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of interest is the fact that the endo protons at C$_3$ and C$_7$ in **2** lie 0.65 ppm farther upfield than the endo protons of **1**.

The leap-frog effect which occurs when Eu(fod)$_3$ is added to **1** or **2** in CDCl$_3$ is demonstrated by the extrapolated values of ΔEu_i (where Eu/**1** or **2** = 1). For **1**, ΔEu_i (hertz downfield from Me$_4$Si at 60 MHz) = 790 (H$_1$), 373 (H$_2$), 413 (H$_3$), and 256 (H$_4$); for **2**, ΔEu_i (Hz) = 740 (H$_1$), 395 (H$_2$), 406 (H$_3$), and 300 (H$_4$). These NMR observations of **1** and **2** show analogy to the case of bicyclo[3.1.0]hex-3-ene-2-one (**18**), where NMR work by Hasty has shown that the α-methine cyclopropyl proton appeared at δ 2.38.[14]

The significantly greater sensitivity of the syn ketone to acid-catalyzed isomerization is a strong indication that the carbonium ion with the syn configuration is either more easily formed or that it *rearranges* more rapidly than the anti carbonium ion, which has already been examined by Gajewski and Shih. In contrast, we found that the carbenes generated by thermolysis of the tosylhydrazone sodium salts of **1** and **2** showed remarkably similar behavior.[2]

Experimental Section

IR spectra were recorded on Perkin-Elmer Model 137 or 437 spectrometers. ^{1}H NMR spectra were obtained using Varian Model A-60-A and XL-100 spectrometers. Mass spectra were obtained using either a Hitachi Perkin-Elmer RMU-6E or an AEI MS 30 mass spectrometer. UV spectra were obtained on a Cary 15 spectrometer and elemental analyses were determined by Atlantic Microlab, Inc., Atlanta, Ga. GC work was carried out using a Varian Aerograph Model A-90-P3 gas chromatograph.

2,2-Diallyl-1,3-dioxolane (9). A solution of 6.95 g (0.0631 mol) of hepta-1,6-dien-4-one (**8**)[4] in 70 mL of benzene was mixed with 5.15 g (0.0830 mol) of ethylene glycol and 0.05 g of *p*-toluenesulfonic acid

monohydrate in a 200 mL round-bottom flask. The flask was fitted with a Dean-Stark trap and a condenser (equipped with a drying tube). The mixture was refluxed until 1.1 mL of water had been collected (97% of the theoretical amount). The cooled reaction mixture was washed with 20 mL of 10% sodium hydroxide solution followed by five 10-mL washes with water. The benzene extract was dried over anhydrous K_2CO_3 and the benzene removed by rotary evaporation. The residual liquid was distilled at 20 mm, affording 4.88 g (0.0316 mol) of **9** (50%): bp 75–76 °C; IR (film) 3040, 3030, 2875, 1645, 1430, 1320, 1300, 1285, 1265, 1240, 1200, 1175, 1140, 1115, 1081, 1040, 1000, 990, 920 cm^{-1}; NMR ($CDCl_3$) δ 2.39 (d with splitting, J = 7 Hz, 4 H), 3.90 (s, 4 H), 4.81–5.28 (AB m, terminal vinyl H, 4 H), 5.47–6.10 (m, 2 H); MS m/e 154 (M^+), 113 ($M^+ - C_3H_5$, major peak).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.35; H, 9.11.

***cis*- and *trans*-3,4-Bis(chloromethyl)cyclopentanone (11).** A mixture of 6.75 g (0.0437 mol) of **9** and 12.1 g (0.0440 mol) of iodobenzene dichloride[5] in 75 mL of chloroform was heated at reflux for 2 h under a slow stream of nitrogen. The chloroform solvent was removed by rotary evaporation, affording a slightly colored mixture containing iodobenzene and crude *cis*- and *trans*-7,8-bis(chloromethyl)-1,4-dioxaspiro[4.4]nonane. The iodobenzene was removed at 0.25 mm while heating the flask to 45 °C. Short-path distillation of the product [bp 88–95 °C (0.25 mm)] afforded 6.80 g (0.0302 mol, 69%) of a brown tinted product.

The crude product (6.75 g, 0.0300 mol) was dissolved in 70 mL of 3:1 ethanol–water containing 200 mg of *p*-toluenesulfonic acid. The solution was heated at 35–38 °C for 24 h. The solution was poured into 500 mL of a saturated Na_2CO_3 solution and extracted with three 200-mL portions of ether. The combined ethereal extracts were washed with water until neutral, followed by a final washing with 100 mL of saturated sodium chloride solution. The ethereal extract was dried over sodium sulfate and concentrated by rotary evaporation, affording 5.11 g of an orange oil. The oil was fractionated through a short-path distilling head (hydroquinone stabilizer), affording the desired dichloro ketone **11**: 2.42 g (0.0134 mol, 45%); IR (film) 2970, 2920, 1755, 1445, 1410, 1370, 1275, 1170, 1100, 770, 735 cm^{-1}; NMR ($CDCl_3$) δ 2.17–2.58 (m, 4 H), 2.58–3.21 (m, 2 H), 3.57–3.80 (overlapping d, $J_{cis} = J_{trans}$ = 6 Hz, 4 H); MS m/e 185 ($M^+ + 4$; 11.1% of M^+), 183 ($M^+ + 2$; 66.2% of M^+), 181 (M^+), 103 ($M^+ - C_3H_7Cl$, major peak).

***syn*- and *anti*-Tricyclo[4.1.0.0^{2,4}]heptan-5-ones (1 and 2). Method A.** A 2.42-g (0.0134 mol) mixture of crude *cis*- and *trans*-**11** was added dropwise to a well-stirred 215 mL 50% sodium hydroxide solution in a 250 mL three-neck flask equipped with a short-path distilling head and a steam inlet (gas bubbler). After stirring for 30 min (reaction mixture had become black), a slow stream of steam was introduced accompanied by gradual heating of the dark reaction mixture to 150 °C (oil bath). The reaction mixture was heated for a minimum of 2 h, periodically introducing 3–4 mL of water to maintain the solvent level. The oil–water distillate was extracted with three 100-mL portions of ether, and the ethereal extract was dried over $MgSO_4$. Concentration by rotary evaporation afforded a light yellow oil (1.15 g), which was distilled to afford 0.83 g of a colorless oil, boiling at 37–42 °C (0.25 mm). The oil (0.00769 mol, 57%) proved to be a clean mixture of the syn (52%) and anti (48%) tricyclic ketones **1** and **2** by GC on a 10 ft × 0.25 in, 10% Carbowax 20M column containing 3.5% KOH (column, 150 °C; He flow, 100 mL/min). The retention times were 15.7 (anti) and 19.6 min (syn). Anti isomer **2**: mp 41.0–42.0 °C (sealed capillary); IR (CCl_4) 2980, 1790 (sh), 1720 (s), 1440, 1340, 1925, 1190, 1145, 1100 (w), 1075 (w), 1050, 1030, 955 (s), 935 (s), 860 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 0.85 (unsymmetrical q, J = 3.5 Hz, 2 H), 1.25 (m, 2 H), 1.56 (m, 2 H), 2.08 (m, 2 H); UV (ethanol) λ_{max} 287 nm (ϵ 28); MS m/e 108 (M^+), 79 ($M^+ - COH$, major peak).

Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.61; H, 7.45.

Syn isomer **1**: IR (film) 2980, 1795 (sh), 1700 (s), 1455, 1313 (sh), 1285, 1185, 1150 (w), 1085 (w), 1040, 1015, 950, 940, 925 (w), 910, 825, 800 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 0.76 (m, 2 H), 1.50 and 1.78 (two overlapping multiplets, 4 H), 2.18 (m, 2 H); UV (ethanol) λ_{max} 283 nm (ϵ 70); MS m/e 108 (M^+), 79 ($M^+ - COH$, major peak).

Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.60; H, 7.53.

***cis*- and *trans*-1-Diazomethylketo-2-vinylcyclopropanes (15).** A solution of 25.8 g (0.460 mol) of potassium hydroxide in 43 mL of water, 150 mL of diethylene glycol monoethyl ether, and 35 mL of ether was placed in a 500 mL Claisen flask equipped with a dropping funnel, a condenser, and two 500 mL Erlenmeyer receivers employing the basic set-up described for diazomethane generation.[15] The flask was heated at 65–70 °C in a water bath while a 92.5-g (0.432 mol) solution of Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide; Aldrich) in 450 mL of ether was added dropwise over a period of 90 min. The ethereal diazomethane (~12.9 g, 0.307 mol) was dried over KOH for 90 min at 0 °C. A solution of cis and trans acid chlorides **14** (10.0 g, 0.0763 mol)[8] in 20 mL of ether was added quickly dropwise to the dried ethereal diazomethane, and the resulting solution was allowed to stir overnight at 25 °C. The yellow ether solution was concentrated by rotary evaporation, giving an orange-yellow oil (~10.0 g, 0.0735 mol) which was employed directly in the next step: IR (film) 3030, 2940, 2100 (s), 1720, 1640 (s), 1440, 1390 (s), 1325 (s), 1205, 1180, 1165 (s), 1100 (s), 1075 (s), 1040, 995, 965, 910 (s), 885, 840, 815, 785, 770, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.75–2.28 (two overlapping m, 4 H), 4.77–5.84 (m, vinyl H, 3 H), 5.31 (s, diazomethyl H, 1 H).

***syn*- and *anti*-Tricyclo[4.1.0.0^{2,4}]heptan-5-ones (1 and 2). Method B.** The crude diazo ketone **15** (10.0 g, 0.0735 mol) was dissolved in 100 mL of cyclohexane and added dropwise over a period of 2 h to a refluxing slurry of 400 mL of cyclohexane and 25 g of anhydrous $CuSO_4$. Upon completion of the addition and further stirring for 1 h under reflux, the slurry was filtered and concentrated via rotary evaporation to afford an orange-red oil. The oil was fractionated (short-path column), giving a fraction (slightly yellow) boiling at 35–44 °C (0.5 mm) and weighing 2.95 g. NMR spectral inspection indicated that the distillate was composed of the desired **1** and **2** contaminated with byproducts possessing the vinylcyclopropane skeleton. Preparative GLC on the above-mentioned KOH-treated column afforded analytically pure samples of the isomeric tricyclic ketones. Column chromatography on silica gel (described below) afforded 1.01 g (0.00935 mol) of separated **1** and **2** (32% from the cis acid chloride). The syn/anti ratio was 47:53.

Purification and Separation of 1 and 2. A crude 7.50-g mixture (distillate from several runs) of **1** and **2** obtained from reaction method B (diazo ketone route) was chromatographed on 200 g (56 cm column height) of silica gel (MCB, G. 62) by eluting (dropping rate, 15 drops/min) with ~900–950 mL of carbon tetrachloride, which both removed major impurities and effected the separation of **1** and **2**. The faster moving syn isomer was stripped from the column by elution with 600 mL of 1:1 carbon tetrachloride–methylene chloride followed by ~400 mL of methylene chloride, which served as a transition solvent between **1** and **2** (the use of methylene chloride required monitoring of the eluent by GC). The appearance of the anti isomer was accompanied by elution with ether, which flushed the slower moving isomer from the column. Final purification of the separated isomers was achieved by short-path distillation, which removed traces of colored materials. The syn distillate proved to be absolutely free of the anti isomer, while the anti distillate contained 2.3% of the syn isomer (by GC). The syn/anti distribution was 1.20 g:1.36 g (47:53). The syn/anti mixtures obtained from reaction method A [bis(chloromethyl) ketone route] were separated in the same manner; a final distillation was found to be unnecessary since the distilled starting mixture of isomers was cleaner than the mixture obtained from method B.

Eu(fod)$_3$ Shifts in the ^{1}H NMR Spectra of *syn*- and *anti*-Tricyclo[4.1.0.0^{2,4}]heptan-5-ones. Proton Assignment. Treatment of 0.8-mL deuteriochloroform solutions of **1** (0.0470 g, 4.35×10^{-4} mol) and **2** (0.0789 g, 7.31×10^{-4} mol) with Eu(fod)$_3$ in varying molar ratios produced interesting lanthanide-induced shifts in the 60 MHz ^{1}H NMR spectra. Assuming the lanthanide atom to lie at a 3.0 Å distance from the oxygen atom (of each respective isomer) in the plane bisecting each system, the various lanthanide–proton distances and proton–Eu–C_5 angles were determined manually from a Dreiding model. Rough calculations of the agreement factor R[13] employing shift data at maximum role ratios afforded R = 0.16 for **1** and R = 0.23 for **2**. Based upon these rough calculations of R and the observed lanthanide-induced shifts in the ^{1}H NMR spectra, the proton assignments of **1** and **2** were established for the 100 MHz spectrum as follows. **1**: δ 0.76 (exo H_4), 1.50 (endo H_3), 1.78 (H_1), 2.18 (H_2). **2**: δ 0.85 (endo H_3), 1.25 (exo H_4), 1.56 (H_1), 2.08 (H_2).

***anti*-Tricyclo[4.1.0.0^{2,4}]heptan-5-one (2). Method C.** Oil-free sodium hydride (0.80 g, 0.033 mol) was added to 50 mL of anhydrous Me_2SO (distilled from CaH_2) in a 100 mL three-neck flask equipped with a solid addition funnel, a condenser, a liquid dropping funnel, and a N_2 inlet. To the mixture was added 7.60 g (0.0345 mol) of trimethylsulfoxonium iodide pinchwise. The resulting solution was allowed to stir for 30 min at 25 °C, whereupon 2.81 g (0.0299 mol) of bicyclo[3.1.0]hex-3-en-2-one (**18**)[9,10] in 10 mL of anhydrous Me_2SO was added slowly dropwise. The solution became orange-brown in color and was stirred at 25 °C for 2 h followed by heating at 55–60 °C for 30 min. The solution was poured into 250 mL of H_2O and extracted with three 150-mL portions of ether. The ethereal extracts were washed with 100 mL of saturated NaCl solution and dried over

Na_2SO_4. Filtration and concentration via rotary evaporation of the ether solution afforded an orange oil (2.74 g) which was distilled through a short-path column at 0.25 mm (bp 36–38 °C). A 2.14-g (0.0198 mol, 66%) fraction of **2** (white solid) was obtained which partially clogged the condenser and receiver elbow, mp 40.5–41.5 °C. GC analysis on the KOH-treated column showed the syn/anti ratio to be 2.2:97.8.

Preparation of Tosylhydrazones. The lability of **1** and **2** in the presence of acid precluded acid-catalyzed formation of the respective tosylhydrazones. The respective tosylhydrazones were prepared by stirring equimolar quantities of *p*-toluenesulfonyl hydrazide and the ketone in absolute ethanol (1 g/25 mL) for 21–24 h (25 °C). A notable exception was **1**, which within 5 min after mixing led to the precipitation of the desired tosylhydrazone; the resulting slurry was stirred for only 2 h before workup. The crude tosylhydrazone obtained from **2** upon removal of solvent was first chromatographed on silica gel (methylene chloride eluent) and then recrystallized from ethanol at 0 °C. The tosylhydrazone from **1** required only recrystallization from ethanol. *syn*-Tricyclo[4.1.0.0^{2,4}]heptan-5-one tosylhydrazone: 83% yield; mp 176.0–178 °C dec; IR (KBr) 3350, 3150, 1630, 1580 (sh), 1450, 1390, 1370, 1330, 1310, 1295, 1180, 1160 (s), 1085, 1040, 1015, 940, 900, 825, 810, 720, 705 cm^{-1}; NMR ($CDCl_3$) δ 0.78 (m, cyclopropyl methylene H, 4 H), 1.96 (m, cyclopropyl methine H, 4 H), 2.40 (s, CH_3, 3 H), 7.47 (s, –NH, 1 H), 7.58 (AB q, aromatic H, 4 H); MS *m/e* 276 (M^+), 91 ($C_7H_7^+$, major peak).

Anal. Calcd for $C_{14}H_{16}O_2N_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.82; H, 5.84; N, 10.19.

anti-Tricyclo[4.1.0.0^{2,4}]heptan-5-one tosylhydrazone: 31% yield; mp 132–134 °C dec; IR (KBr) 3350, 3150, 2850, 1590 (sh), 1540, 1480, 1430, 1385, 1335, 1320, 1310, 1300, 1180, 1160 (s), 1085, 1025, 1010, 935, 895, 820, 805, 725, 715, 705 cm^{-1}; NMR ($CDCl_3$) δ 0.52 (m, cyclopropyl endo H, 2 H), 1.03 (m, cyclopropyl exo H, 2 H), 1.70 (m, cyclopropyl methine H, 4 H), 2.40 (s, CH_3, 3 H), 7.27 (s, –NH, 1 H), 7.58 (AB q, aromatic H, 4 H); MS *m/e* 276 (M^+), 91 ($C_7H_7^+$, major peak).

Anal. Calcd for $C_{14}H_{16}O_2N_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.82; H, 5.86; N, 10.17.

Registry No.—**1**, 67252-83-9; 1 tosylhydrazone, 67252-84-0; **2**, 28697-20-3; **2** tosylhydrazone, 67252-85-1; **8**, 53859-89-5; **9**, 67194-62-1; *cis*-**11**, 67194-63-2; *trans*-**11**, 67194-64-3; *cis*-**14**, 2183-92-8; *trans*-**14**, 2183-93-9; *cis*-**15**, 67194-65-4; *trans*-**15**, 67194-66-5; **18**, 32264-58-7; *cis*-7,8-bis(chloromethyl)-1,4-dioxaspiro[4.4]nonane, 67194-67-6; *trans*-7,8-bis(chloromethyl)-1,4-dioxaspiro[4.4]nonane, 67194-68-7.

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Chemistry of Carbanions. 33. Use of Intramolecular Alkylation for the Stereospecific Formation of a *cis*-Decalone[1]

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The synthesis of the decalone derivatives **1** and **14** and the related enol acetates **15** and **16** is described. This synthesis utilizes the stereoselective conjugate addition of CH_2=CHMgBr in the presence of a Cu(I) catalyst to form the vinyl ketone **5**. Subsequent addition of HBr in a radical chain reaction followed by regiospecific formation and cyclization of the bromo enolates **12** and **13** formed the desired decalones **1** and **14**.

To continue exploration of the possibility[2] of controlling reaction stereochemistry in polycyclic systems by use of a conformational effect transmitted from a remote bulky substituent, we wished to prepare ketone **1** (Scheme I). We plan to compare the stereochemistry of C-9 alkylation of this ketone **1** with an earlier study[3] of the alkylation of the stereoisomeric ketone **2**. This paper reports a suitable route for the preparation of ketone **1**.

The basic problem in this synthesis was the requirement to establish and maintain the two chiral centers at C-6 and C-10 in the less stable arrangement with the two alkyl groups trans (i.e., one alkyl group axial). Application of a standard Robinson annulation technique to 4-*tert*-butylcyclohexanone (**3**) was clearly inappropriate because equilibration during this process ultimately leads to the more stable ketone **2**.[3] Consequently, we used an alternative procedure[4,5a] in which the ketone **3** was converted to the enone **4** and then allowed to react with CH_2=CHMgBr in the presence of a Cu(I) catalyst (0.1 molar equiv of Me_2SCuBr). This organometallic reagent (CH_2=CHMgBr + 0.1 equiv of Me_2SCuBr) has been found[4b,5a] to react with enones in a manner equivalent to the cuprate, $(CH_2{=}CH)_2CuLi$, that is presently difficult to prepare because of the lack of a commercial source for vinyllithium. By use of these Cu(I) reagents, both methyl and vinyl groups have been found[4,5a] to add to the enone **4** to form mixtures of stereoisomeric ketones (e.g., **5** and **6**) in which the epimers (e.g., **5**) with an axial methyl or vinyl group constitute >90% of the ketone product. We had previously[5a] used a low-temperature recrystallization technique to separate a pure sample of ketone **5a**, the major stereoisomer in the reaction mixture, and have subsequently found that both epimers **5a** and **5b** can be obtained in pure form by low-pressure liquid chromatography. An equilibrium mixture of these two epimers contained ca. 70% of **5a** and ca. 30% **5b**.[4b,5a] Pure samples of the two minor epimeric ketones **6a** and **6b** were also separated by low-pressure liquid chromatography. An equilibrated mixture of these epimers **6** at 25 °C contained 99% of the equatorial isomer **6a** and 1% of the axial isomer **6b**.

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